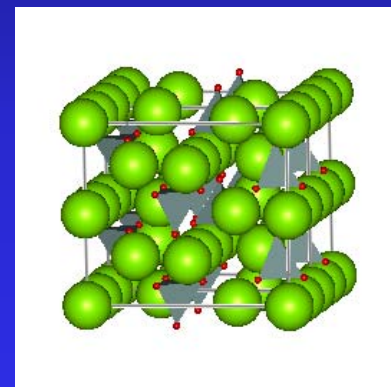
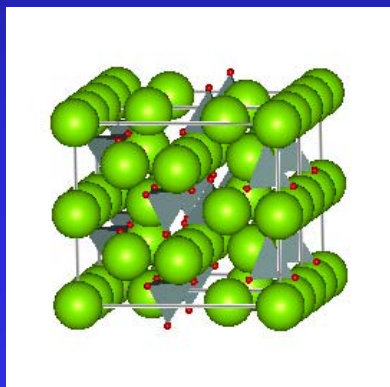


EXPLORING THE MECHANISMS THAT CONTROL OLIVINE CARBONATION REACTIVITY DURING AQUEOUS MINERAL CARBONATION

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CARBON DIOXIDE SEQUESTRATION VIA Mg-RICH MINERAL CARBONATION

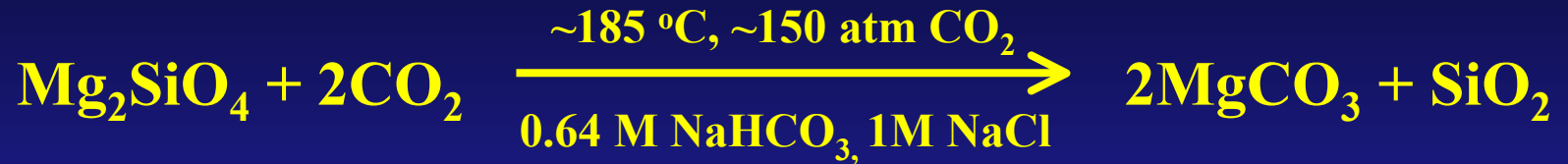
ADVANTAGES

- **The process occurs naturally and yields environmentally benign and geologically stable products (e.g., MgCO_3 and SiO_2).**
- **It offers the capacity for large scale sequestration. Mg-rich minerals are widely available globally as relatively low cost feedstocks (e.g., olivine and serpentine).**
- **It minimizes the ongoing costs associated with long term storage (e.g., site monitoring, leakage, liability, etc.).**
- **Carbonation is exothermic for both serpentine and olivine, enhancing the potential for low-cost process development.**

PRIMARY CHALLENGE

Economically viable process development.

AQUEOUS SOLUTION MINERAL CARBONATION



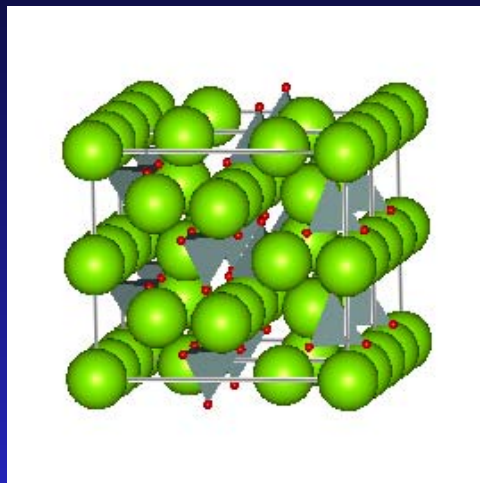
A Promising Process

- Developed by the Albany Research Center
- Accelerated olivine carbonation from geological time to less than an hour.

The Primary Challenge

- Reducing Process Cost
In particular, reducing or eliminating the cost of mineral activation, while enhancing carbonation.

UNDERSTANDING OLIVINE CO₂ MINERAL SEQUESTRATION MECHANISMS AT THE ATOMIC LEVEL



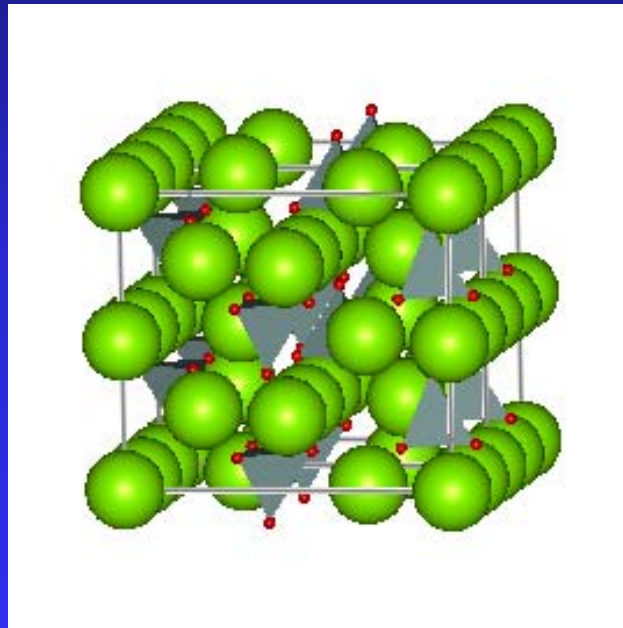
Olivine (forsterite: Mg₂SiO₄)

OBJECTIVE: to explore the materials associated with the ARC aqueous olivine carbonation process down to the atomic level to identify the key mechanisms that govern carbonation reactivity.

GOAL: to develop the necessary mechanistic understanding to facilitate the engineering of improved processes to reduce process cost.

$$\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \longrightarrow 2\text{MgCO}_3 + \text{SiO}_2$$

olivine magnesite ? silica ?



Solid State Volume Change (% of initial volume)

Mg₂SiO₄: 100%

2MgCO₃: 130%

SiO₂: 62%

~ 92% total volume increase

CHARACTERIZATION OF THE SAN CARLOS OLIVINE FEEDSTOCK

Materials Investigated

Single crystals (to 10 mm)
& polycrystalline material

Microprobe Composition Analysis

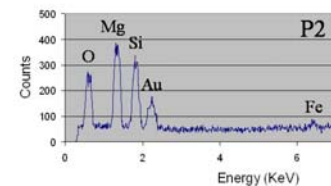
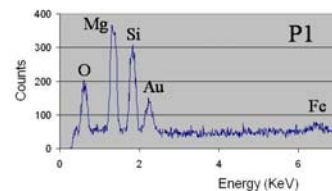
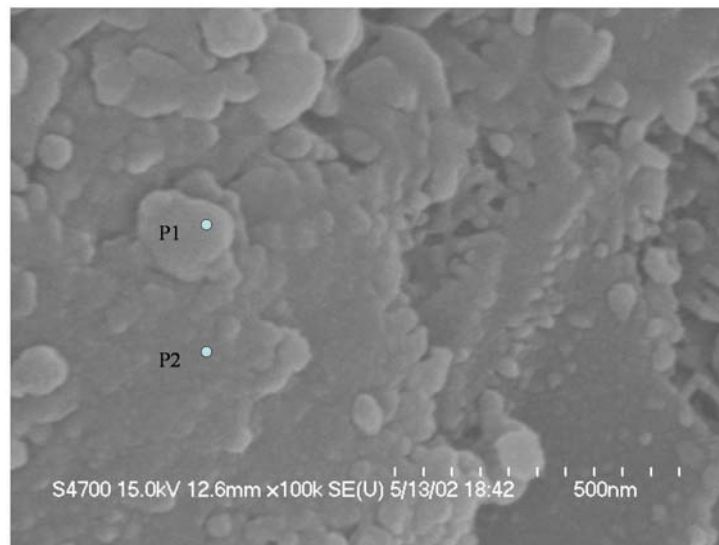
Composition: $(\text{Mg}_{0.92}\text{Fe}_{0.08})_2\text{SiO}_4$
Impurities (oxide): Mn 0.12%; Ca 0.11%.

XPD Structural Analysis

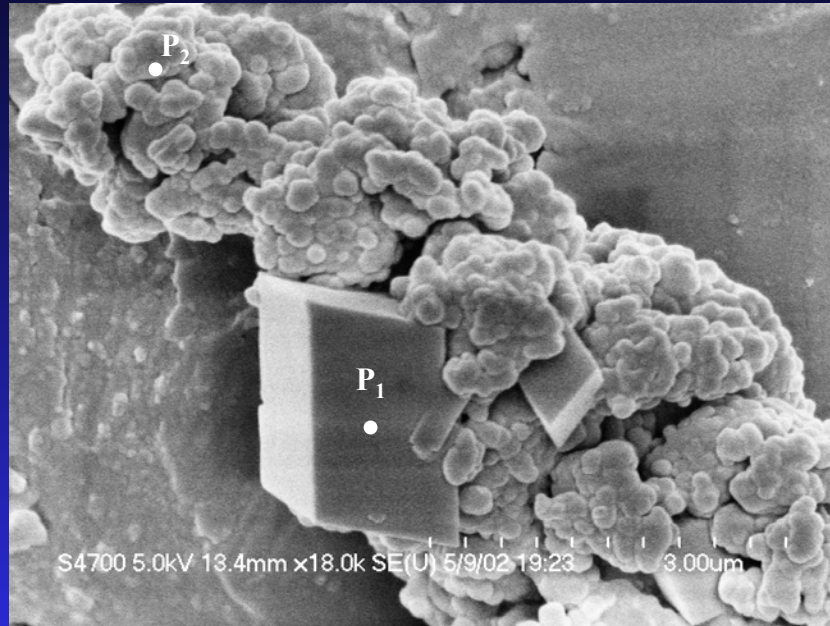
Orthorhombic

$a = 4.763 \text{ \AA}$; $b = 10.223 \text{ \AA}$; $c = 5.993 \text{ \AA}$

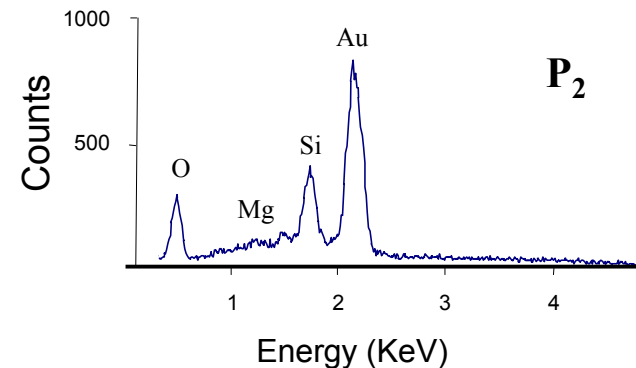
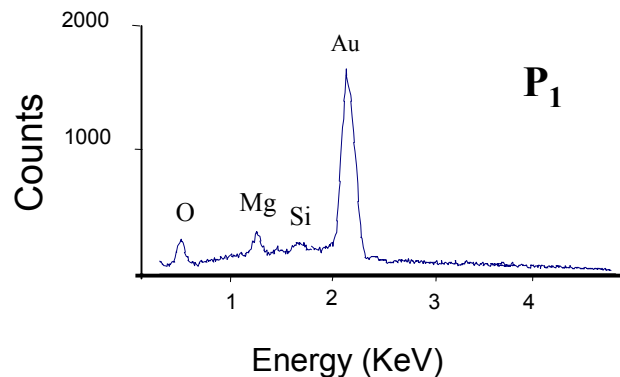
FESEM EDS Analysis



FESEM ENERGY DISPERSIVE X-RAY ANALYSIS OF OLIVINE CARBONATION REACTION PRODUCTS*



***1,500 rpm stirring**

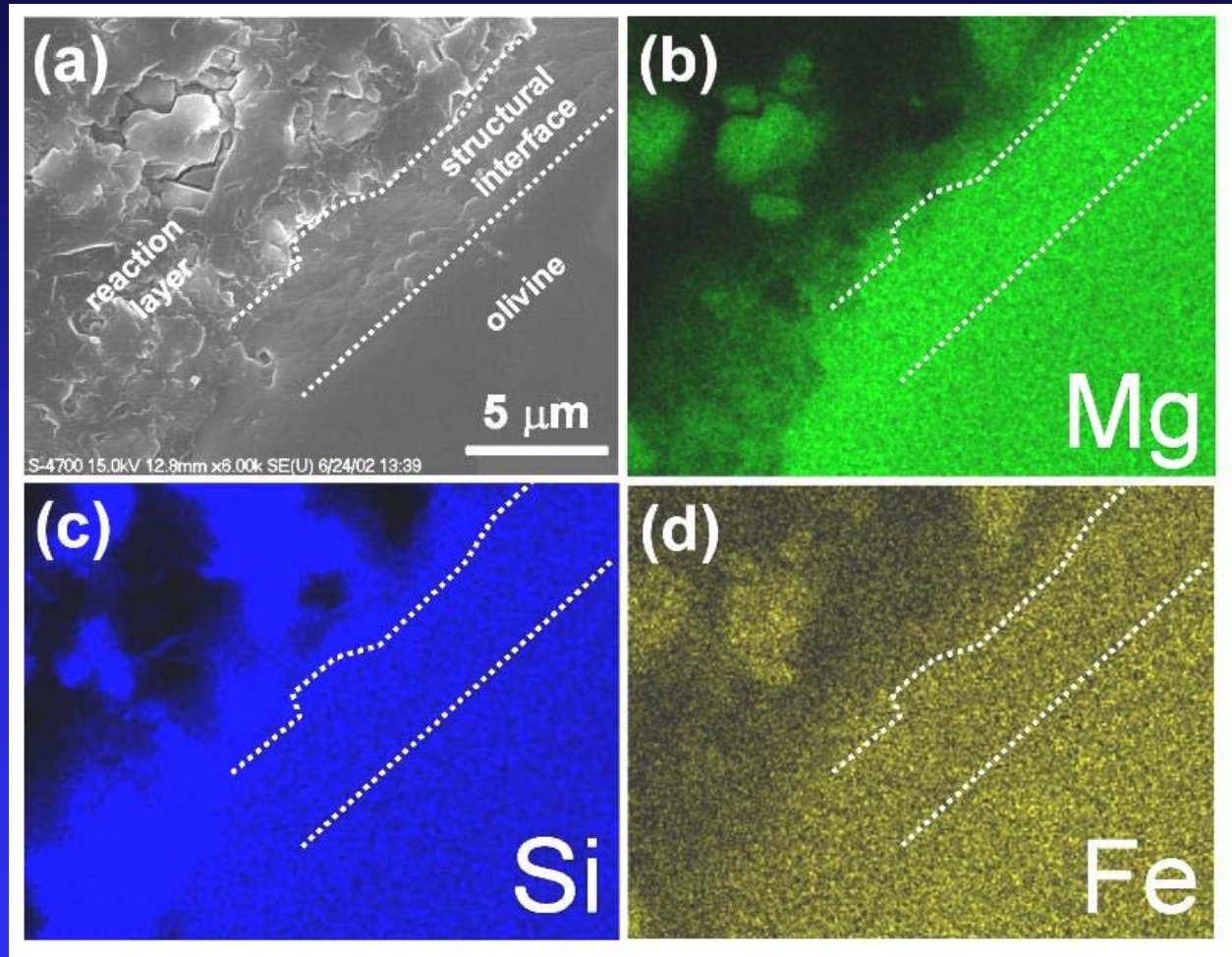


SILICA LAYER FORMATION & MAGNESITE INTERGROWTH WITH THE PARTIALLY CARBONATED OLIVINE MATRIX*



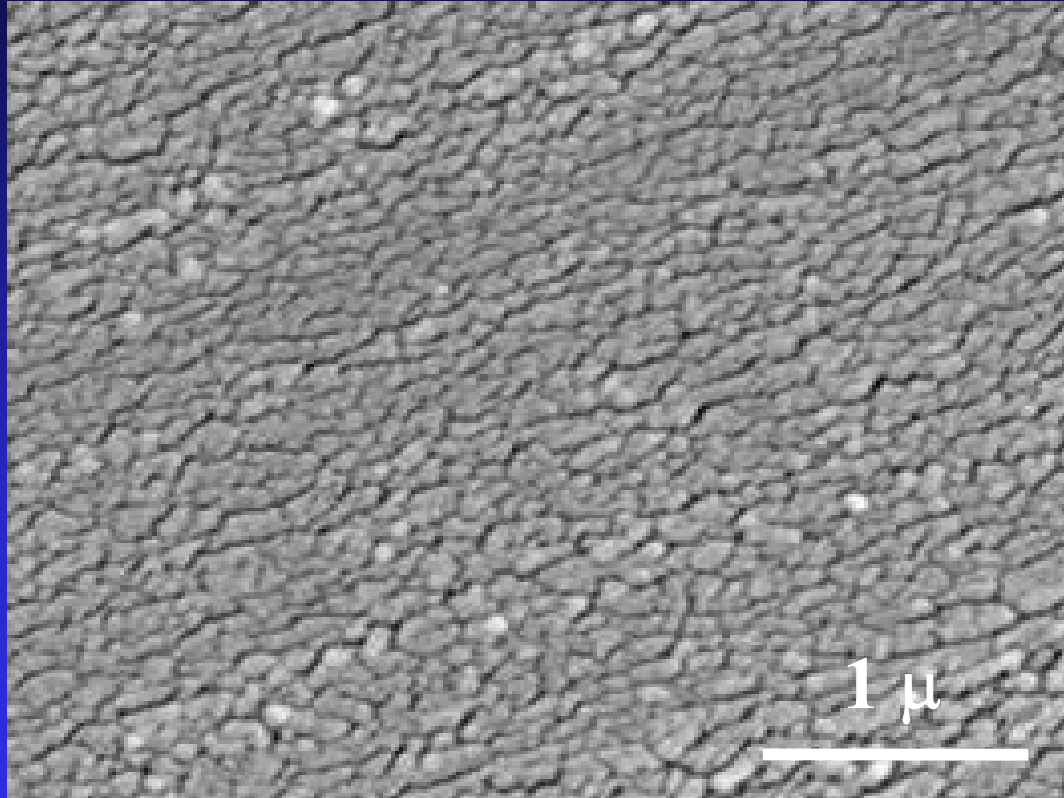
*1,500 rpm stirring

STRUCTURAL DISRUPTION PRECEDES CARBONATION AT THE OLIVINE REACTION FRONT*



*1,500 rpm stirring

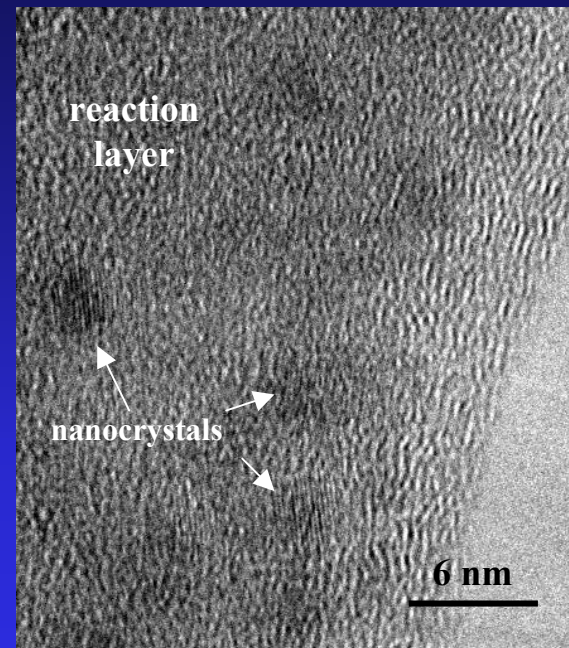
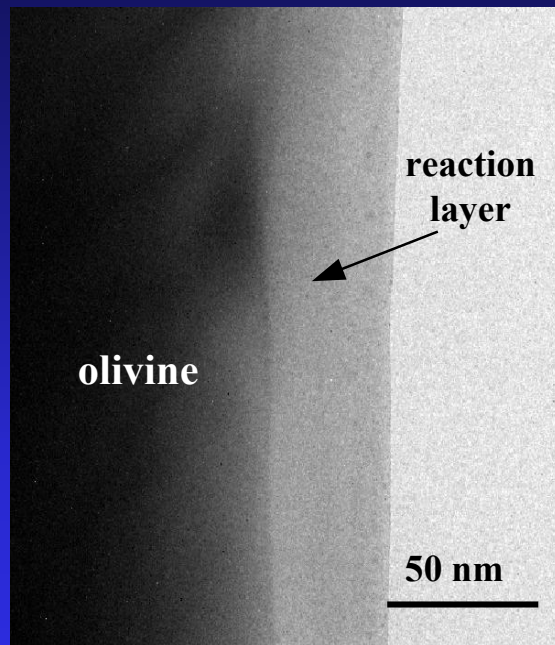
SILICA-RICH SURFACE LAYER FORMATION DURING UNSTIRRED OLIVINE CARBONATION*



Note the cracking of the surface consistent with a system under tension.

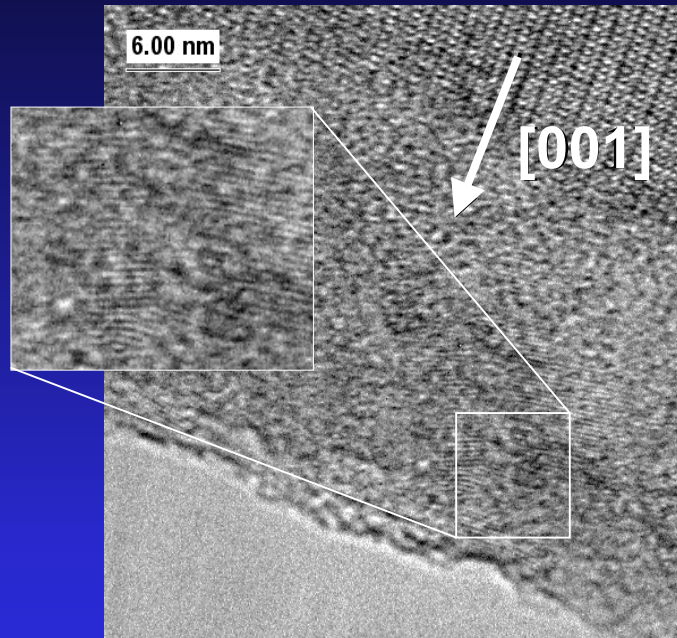
*** 2 hour reaction without stirring**

CROSS SECTION OF THE SILICA-RICH PASSIVATING LAYER THAT FORMS WITHOUT STIRRING

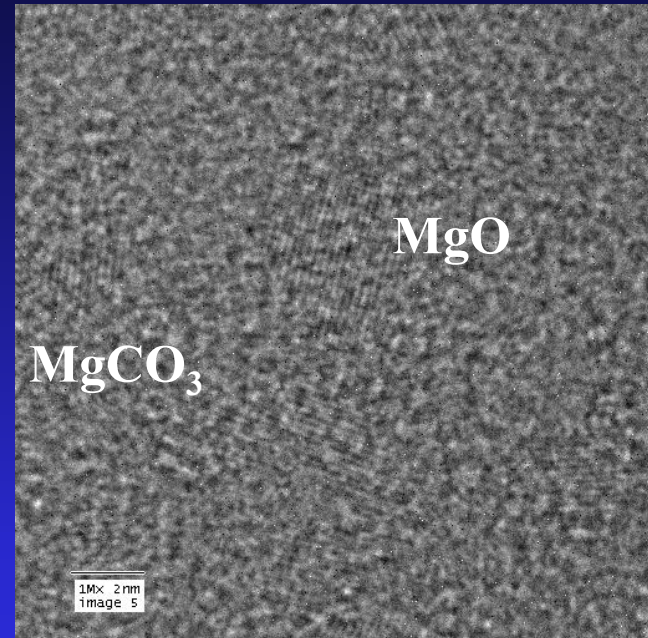


Nanoscale TEM image of the olivine/silica-rich reaction interface that forms after one hour, as viewed between the surface cracks observed via FESEM.

MAGNESITE NANOCRYSTAL FORMATION IN THE SILICA-RICH PASSIVATING LAYERS

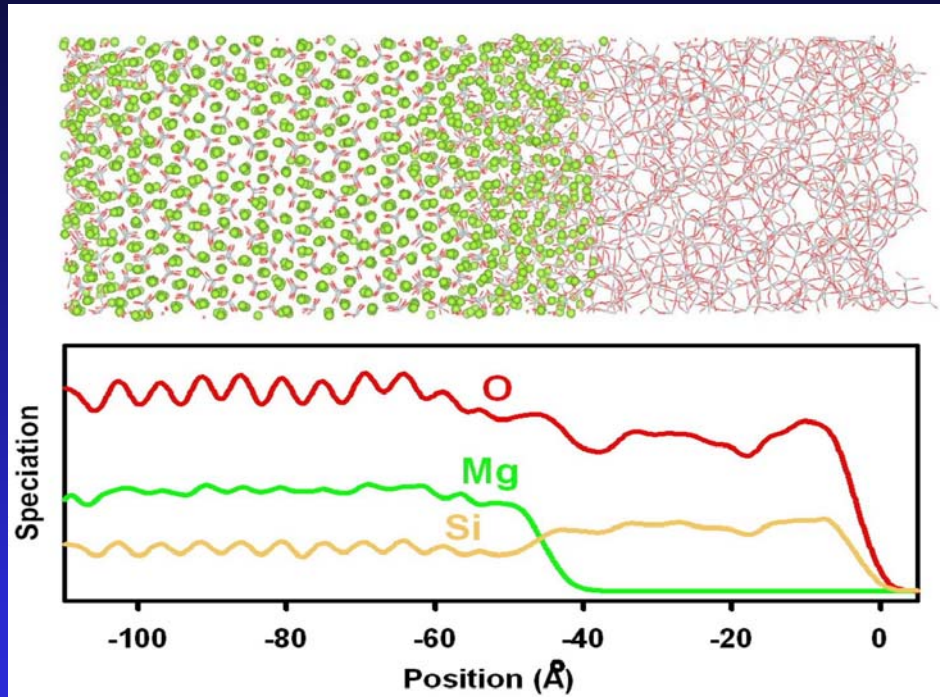


A high-resolution HRTEM image of nanocrystals that form in the silica-rich passivating layers during mineral carbonation.

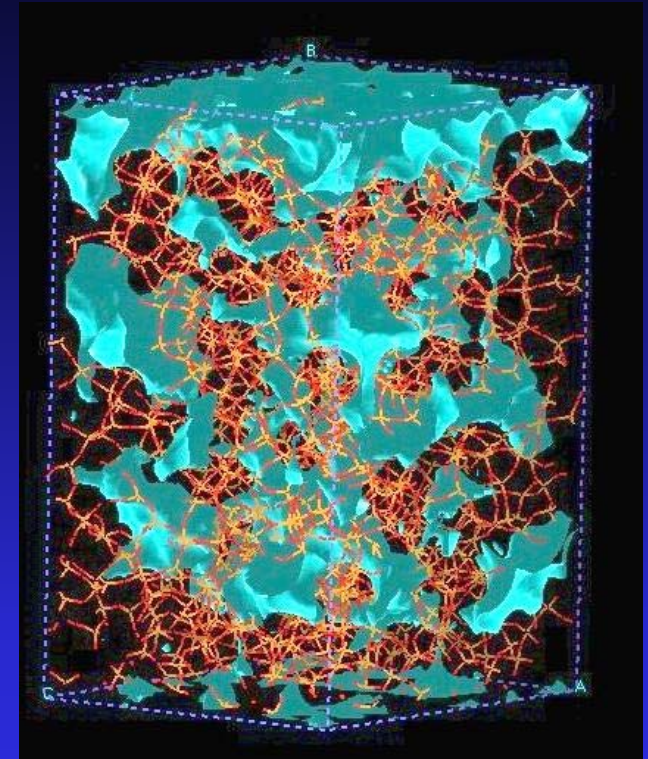


High resolution image of MgCO₃ and MgO nanocrystals observed in the disordered silica-rich passivating layer. MgCO₃ decomposes in the electron beam to give the MgO particles observed.

ATOMIC LEVEL SIMULATION OF SILICA-RICH PASSIVATING LAYER STRUCTURE

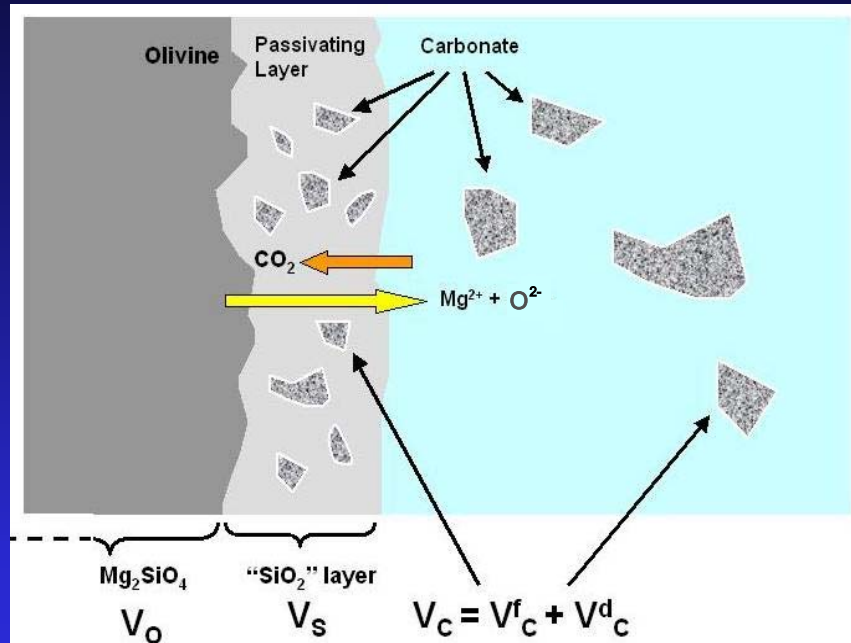


10,000 atom simulation of the passivating layer structure showing a continuous reaction front between olivine and an amorphous “SiO₂”-like nanoporous passivating layer.



Map of nanoscale pore distribution and structure within the passivating layer. Enhanced product and reactant diffusion is promoted by continuous channels. Nanoscale voids may provide nucleation sites for MgCO₃ growth.

CONCEPTUAL MODEL OF PASSIVATING LAYER FORMATION, STRUCTURE AND STRAIN STATE



Schematic of the passivating layer formation process

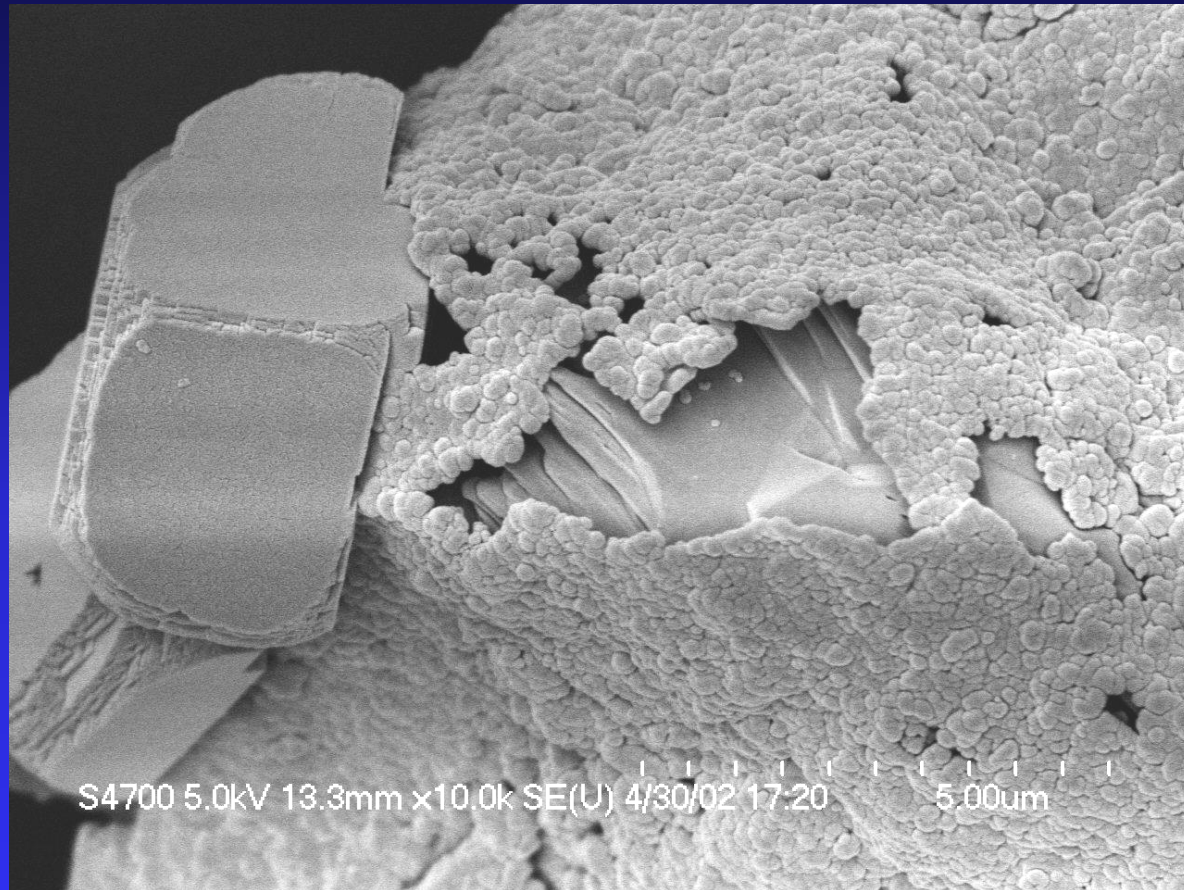
% MgCO_3 free	% MgCO_3 In layer	$\frac{V(\text{products})}{V(\text{reactants})}$	Strain State of layer	MgCO_3 % Volume in layer
0%	100%	1.91	compression	67 %
10%	90%	1.78	compression	65 %
20%	80%	1.65	compression	62 %
30%	70%	1.52	compression	59 %
40%	60%	1.39	compression	55 %
50%	50%	1.26	compression	51 %
60%	40%	1.13	compression	45 %
70%	30%	1.01	compression	38 %
80%	20%	0.88	tension	29 %
90%	10%	0.75	tension	17 % *
100%	0%	0.62	tension	0 %

* HRTEM

Calculated strain state of the passivating layer based on bulk molar volume data

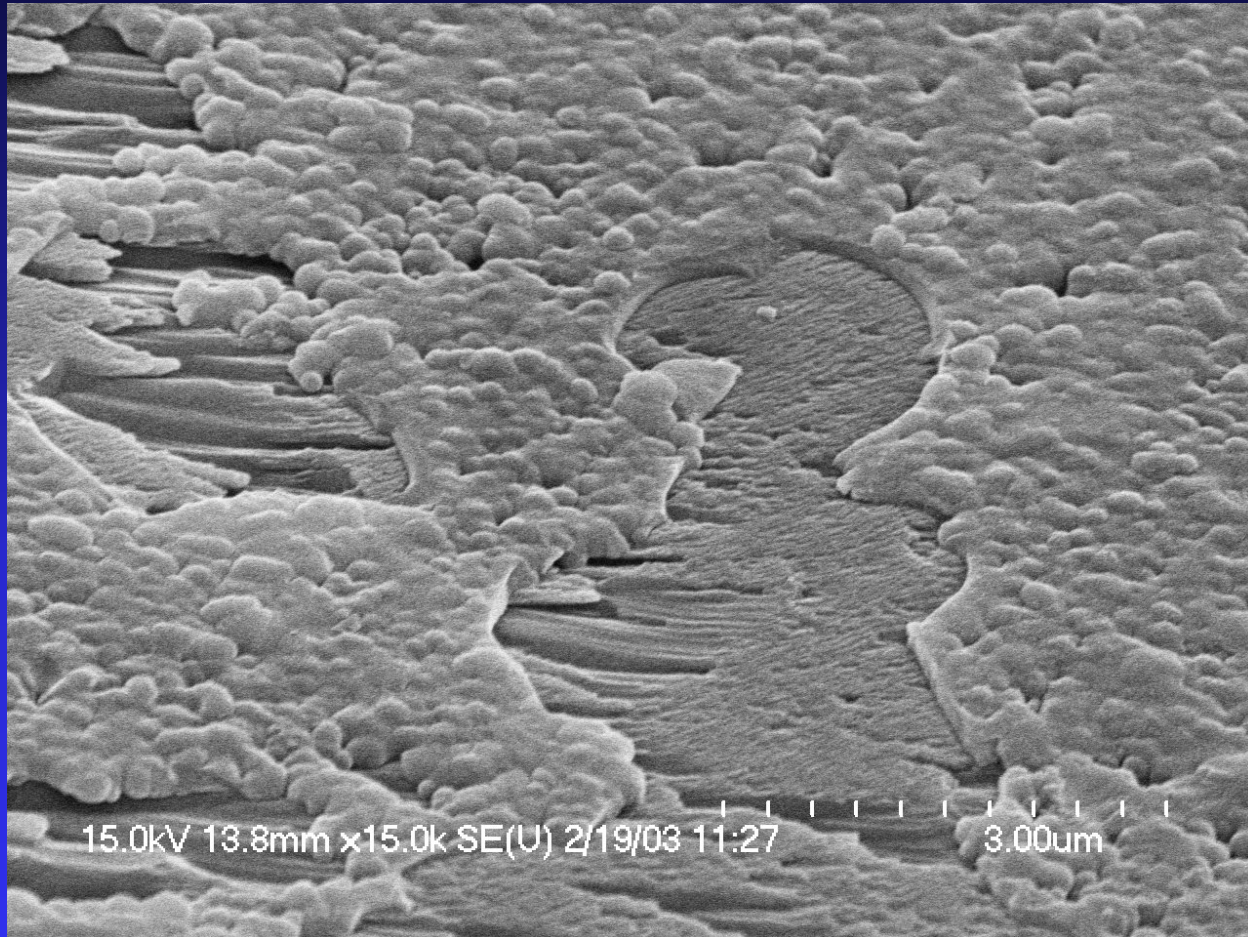
**WHAT IS THE ROLE OF PASSIVATING
LAYER FORMATION/EXFOLIATION
DURING STIRRED MINERAL
CARBONATION?**

SILICA-RICH LAYER FORMATION AND SURFACE ABRASION OF INTERGROWN MAGNESITE CRYSTALS*



*1,500 rpm stirring

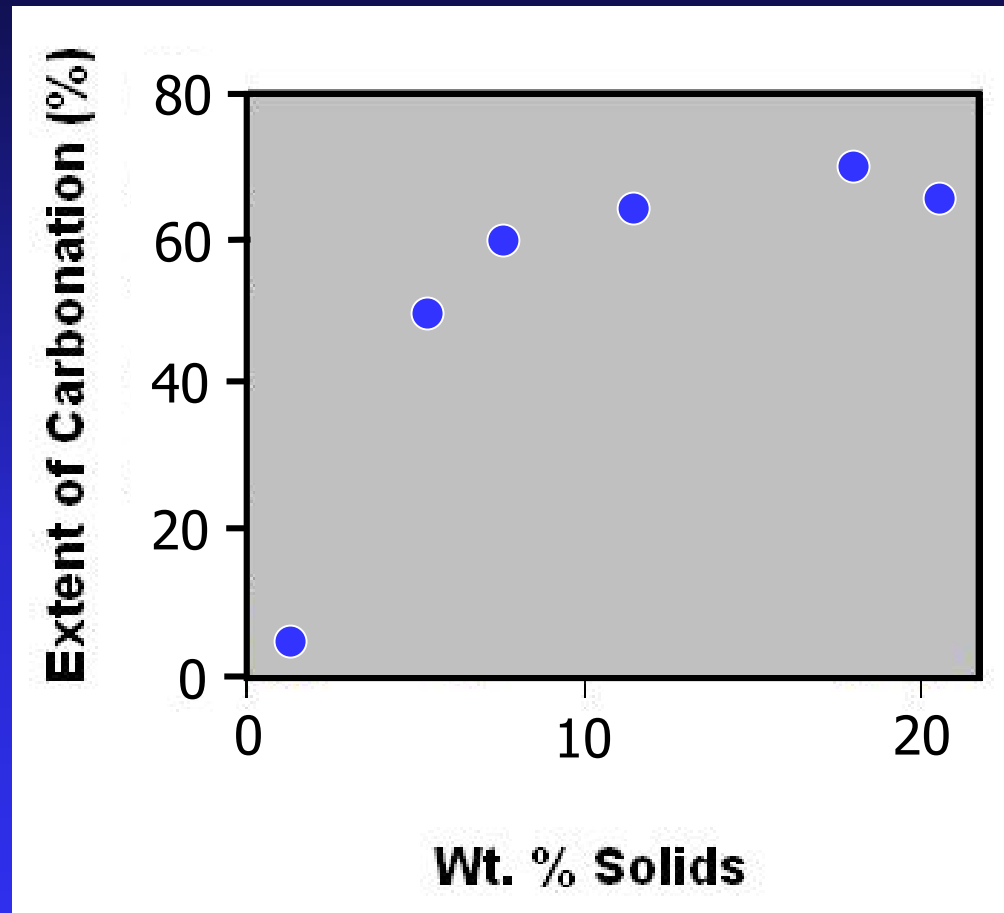
SILICA-RICH LAYER FORMATION: ABRASIVE REMOVAL AND REGROWTH



***1,500 rpm stirring**

**CAN CARBONATION BE ENHANCED
BY PROMOTING PASSIVATING
LAYER EXFOLIATION ?**

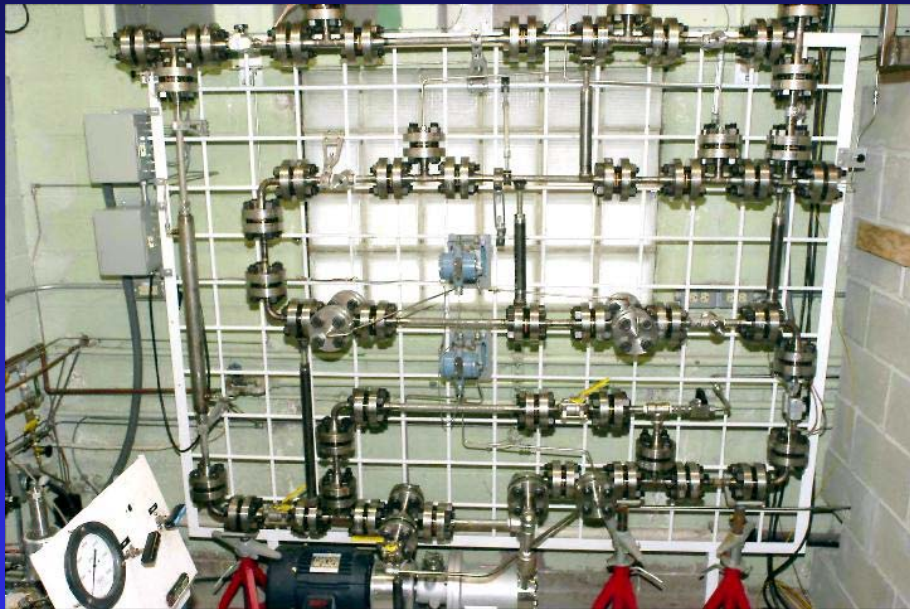
EXTENT OF CARBONATION AS A FUNCTION OF WT % SOLIDS PRESENT DURING MINERAL CARBONATION*



* Carbonation of synthetic forsterite @ 185 °C, 150 atm CO₂, with 1,500 rpm stirring for 1hr.

OBSERVATIONS OF ENHANCED OLIVINE CARBONATION IN THE ARC FLOW LOOP REACTOR

(Albany Research Center: Penner, O'Connor, Gerdemann, Dahlin, et al.)



- **Dramatic increase in carbonation observed for the flow-loop reactor:**
autoclave: <10% carbonation
loop reactor: 72% carbonation
- **Strong correlation between enhanced reactivity and the degree of turbulence**
- **Reactivity remains high even for untreated, large-grain feedstock.**

Table 1- Effect of Pump Speed on Extent of Carbonation (with mixers)		
Pump Speed, rpm	Grind size	With Mixers - Extent of Reaction, %
1198	< 200 mesh	63.2
1450	< 200 mesh	73.8
1002	< 200 mesh	66.9
1750	< 200 mesh	77.9
Pump Speed, rpm	Grind size	No Mixers - Extent of Reaction, %
1198	< 200 mesh	37.5
1002	< 200 mesh	47.1

CONCLUSIONS

- Olivine mineral carbonation is a complex process, which yields magnesite and amorphous silica.
- Silica-rich passivating layers form on the olivine reaction surface during carbonation.
- Magnesite nanocrystals nucleate and grow in these layers during the carbonation process.
- Disruption of the passivating layers offers exciting potential for dramatically enhancing carbonation reactivity, while avoiding the cost of mineral pretreatment activation.

FUTURE WORK

Objective: to identify key parameters that can enhance olivine carbonation, while avoiding the cost of pretreatment activation.

Approaches include:

- multi-phase fluid modeling and experimental investigations that elucidate key fluid-flow parameters and slurry interactions that can enhance exfoliation,
- chemical studies that probe the potential aqueous cation size (e.g., Li^+ , Na^+ , and K^+) offers to mitigate passivating layer effectiveness and enhance exfoliation, and
- investigations that elucidate the potential that sonication offers to enhance exfoliation and particle cracking.

Advanced experimental and computational modeling investigations will be integrated with the above studies to develop an atomic-level understanding of the associated mechanisms that control passivating layer exfoliation and carbonation reactivity.